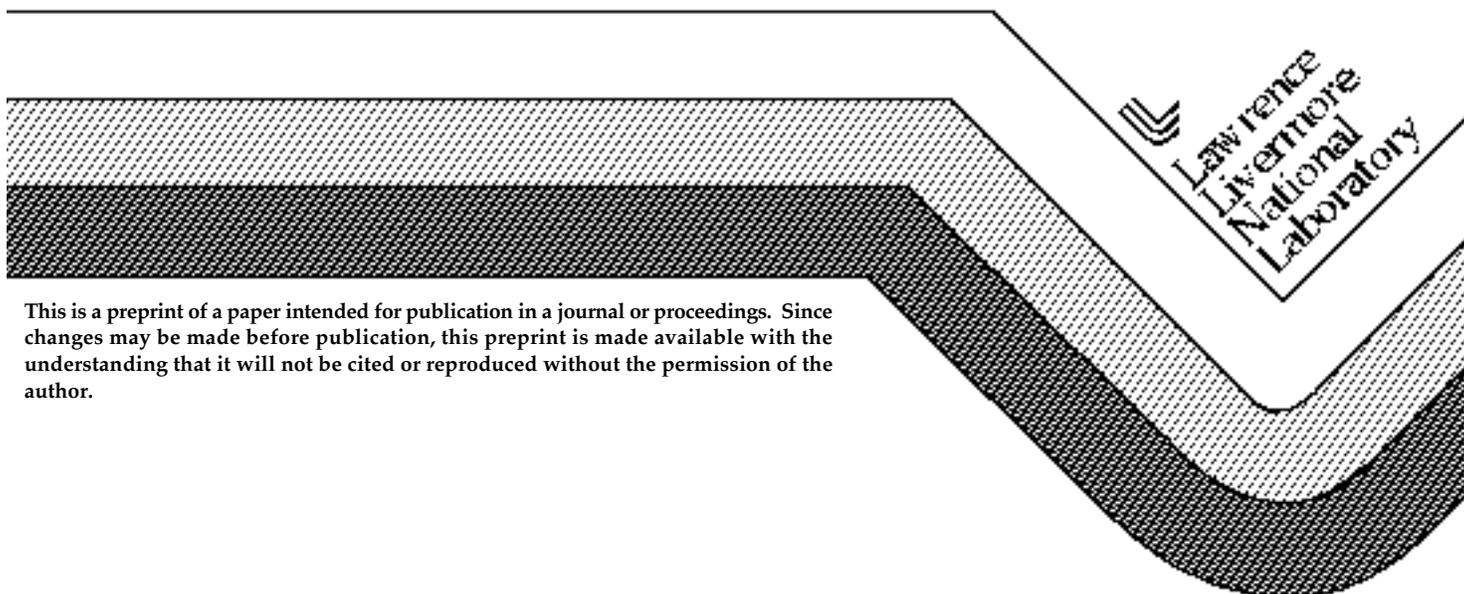


A Monte Carlo Simulation Method for Assessing Biotransformation Effects on Groundwater Fuel Hydrocarbon Plume Lengths

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Abstract

Biotransformation of dissolved groundwater hydrocarbon plumes emanating from leaking underground fuel tanks should, in principle, result in plume length stabilization over relatively short distances, thus diminishing the environmental risk. However, because the behavior of hydrocarbon plumes is usually poorly constrained at most leaking underground fuel tank sites in terms of release history, groundwater velocity, dispersion, as well as the biotransformation rate, demonstrating such a limitation in plume length is problematic. Biotransformation signatures in the aquifer geochemistry, most notably elevated bicarbonate, may offer a means of constraining the relationship between plume length and the mean biotransformation rate. In this study, modeled plume lengths and spatial bicarbonate differences among a population of synthetic hydrocarbon plumes, generated through Monte Carlo simulation of an analytical solute transport model, are compared to field observations from six underground storage tank (UST) sites at military bases in California. Simulation results indicate that the relationship between plume length and the distribution of bicarbonate is best explained by biotransformation rates that are consistent with ranges commonly reported in the literature. This finding suggests that bicarbonate can indeed provide an independent means for evaluating limitations in hydrocarbon plume length resulting from biotransformation.

Key Words: Analytical transport modeling, biodegradation, biotransformation, groundwater contamination, Monte Carlo analysis.

1. Introduction

Dissolved fuel hydrocarbons associated with underground storage tanks (USTs) are often observed to biotransform in groundwater under a variety of biogeochemical regimes (Reinhard et al., 1984; Barker et al., 1987; Major et al., 1988; Baedecker et al., 1993; Lovley et al., 1995; Kazumi et al., 1997). As such, groundwater hydrocarbon plumes may undergo some degree of self-remediation that may limit downgradient migration and hence reduce some of the associated exposure risk (Salanitro, 1993; Rice et al., 1995; Mace et al., 1997). Even in the presence of a continuous source of fresh contaminants (e.g., residual free-product), mass loss through biotransformation, integrated across the spatial extent of the plume, will often lead to a pseudo-steady-state condition with regard to plume length (although this may not necessarily be true if biotransforming microorganisms are not present throughout the plume). By this conceptual model, the eventual downgradient extent of such a stable plume, a measure of the risk posed to receptors such as water-supply wells, will depend on the overall rate of biotransformation.

Several techniques have been developed to estimate mean biotransformation rates at individual sites. Familiar examples include exponential regression of measured concentrations as a function of distance downgradient from the source area along the longitudinal axis of the plume under presumed steady-state conditions (Buscheck, Alcantar, 1995) or normalization of biodegrading components by presumed recalcitrant tracers (Wilson et al., 1994a). However, many of these techniques do not take advantage of the information provided by geochemical signatures of biotransformation frequently observed at UST sites. The consumption of electron acceptors (e.g., dissolved oxygen, nitrate, sulfate, ferrous iron and manganese in oxyhydroxide

mineral phases) by oxidative biotransformation reactions is well recognized (Lovley et al., 1989; Haag et al., 1991; Vroblesky, Chapelle, 1994; Borden et al., 1995), as is the accumulation of reaction products such as carbon dioxide, methane, and ferrous iron (Cozzarelli, Baedecker, 1992; Baedecker et al., 1993). Concentration distributions of these species pose mass balance constraints that may be used to refine models of biotransforming fuel hydrocarbon plumes (McNab, Dooher, 1998).

Numerous case studies have demonstrated spatial and temporal relationships between geochemical biotransformation indicators and fuel hydrocarbon concentrations, yet few have attempted to integrate such information from multiple sites in a quantitative, systematic manner. Such an integrated viewpoint may prove to be most useful to policy makers and regulatory agencies that concern themselves with a broad spectrum of sites. The purpose of this study is to gain insight into the relationships between geochemical footprints of biotransformation (specifically, bicarbonate concentrations) and dissolved fuel hydrocarbon plume lengths across multiple sites using a Monte Carlo reactive transport modeling approach. This approach entails generating a population of synthetic fuel hydrocarbon plumes using an analytical solution to the solute transport equation, tallying the resulting probability distributions of plume length and differences in bicarbonate between plume interior and background, and comparing the results to field observations. Probability distributions used to generate each Monte Carlo realization were developed from hydrogeologic data from multiple sites, or, in the case of mean biotransformation rates, postulated from the literature.

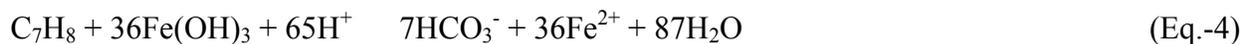
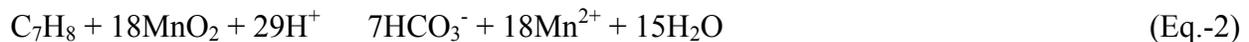
Groundwater quality data were chosen for this study from six UST sites located at existing and former military bases in California (Table 1). These include the Area 43 Gas Station at Camp

Pendleton Marine Corps Base (PMCB), the Petroleum, Oils, and Lubricants Fuel Farm Area at Castle Air Force Base (CAFB) near Merced, the Operable Unit 2 area at George Air Force Base (GAFB) near Victorville, the Building 637 area at the Presidio of San Francisco (PSF), the North-South Gas Station at Travis Air Force Base (TAFB) near Fairfield, and the Base Exchange Service Station at Vandenberg Air Force Base (VAFB) near Lompoc. Data included total petroleum hydrocarbons (TPH) and benzene/toluene/ethylbenzene/xylenes (BTEX) measured by gas chromatography. Geochemical indicator parameters (e.g., nitrate, sulfate, ferrous iron) were typically measured by ion chromatography or atomic adsorption spectroscopy. However, not all of the geochemical indicator data were available from all the sites. Plume lengths at the six sites were defined as the approximate distance from the source area to the downgradient edge of the TPH plume at the 10 parts-per-billion (ppb) contour level.

2. Modeling Approach

2.1. Geochemical Idealization

Ideally, dissolved-phase fuel hydrocarbons may be completely transformed (mineralized) through a variety of microbially-mediated biogeochemical reactions. Neglecting the uptake of carbon by microorganisms for cell growth, such reactions (using toluene as a surrogate fuel hydrocarbon compound) may include:





In most instances, these reactions occur in a sequence that is roughly consistent with thermodynamic constraints, as in the order listed, leading to the development of spatial zonation of biogeochemical regimes. With the exception of methanogenesis (Eq.-6), each electron acceptor utilization reaction yields carbon dioxide as a reaction end product in the same stoichiometric proportion. In the near-neutral pH environments typically encountered in shallow, alluvial settings where UST sites are often found, $\text{CO}_2(\text{aq})$ will exist primarily as bicarbonate, HCO_3^- , which is often measured in groundwater as bicarbonate alkalinity (Drever, 1988). This suggests the possibility of using bicarbonate as a mass balance constraint for biotransformation processes. Although a number of factors will influence bicarbonate in such systems, namely equilibration with carbonate minerals and off-gassing of CO_2 , these are not expected to exert significant effects on carbon mass balance unless conditions are strongly methanogenic.

As a demonstration, the U.S.G.S. geochemical speciation model PHREEQC (Parkhurst, 1995) was used to simulate the titration and subsequent complete mineralization of toluene into a hypothetical groundwater composition characterized by the presence of typical quantities of various electron acceptors (e.g., 8 mg/L dissolved oxygen, 20 mg/L nitrate, 20 mg/L sulfate, solid-phase ferrihydrite). At each stage of the titration, equilibrium was assumed between all redox couples, the aqueous phase was assumed to be in equilibrium with calcite, CaCO_3 , and CO_2 and CH_4 gases were assumed to evolve after the respective fugacities exceeded 0.1 atm.

The resulting carbon mass balance predictions are illustrated on Fig. 1. The assumption that all of the toluene is converted to aqueous-phase CO₂ species (HCO₃⁻, CO₃²⁻, etc.) appears to hold for titrated quantities less than 0.0004 moles/kg of water (i.e., difference between assumed CO₂(aq) and predicted CO₂(aq) is less than 10%). Even at a titration amount of 0.004 moles/kg, the assumed and predicted quantities of CO₂(aq) differ by only a factor of two. Beyond this level, the assumption breaks down because of the predicted evolution of CH₄ and CO₂ gases from the system. Although these predictions are unique to this example, the implication is that bicarbonate may provide a reasonable mass balance constraint on biotransforming fuel hydrocarbons as long as conditions are not too strongly methanogenic.

Median values of geochemical parameter values at each of the six sites included in the study are shown on Table 2. Plume interior wells were defined at each site as those wells containing TPH above the applicable detection limit; remaining wells were defined as background wells. Median values, as opposed to mean values, were chosen as representative values from the two categories to minimize the influence of extreme values. For almost every parameter at every site, differences in median values are consistent with biotransformation processes. Among the six sites as a whole, sulfate reduction appears to be the dominant process, whereas methogenesis, which leads to conditions that violate the bicarbonate mass balance assumption, is limited. If the magnitude of a geochemical indicator signature is defined as,

$$C = C_{plume}^* - C_{bkg}^* \quad (\text{Eq.-7})$$

where c_{plume}^* and c_{bkg}^* refer to the respective median plume interior and median background concentrations, then an inverse relationship should exist between c defined with respect to bicarbonate (an expected positive value) and c defined with respect to sulfate (an expected

negative value). The relationship between *c-bicarbonate* and *c-sulfate* for the six sites, based on Table 2, is shown on Fig. 2, along with the ideal *c* relationship if sulfate reduction (Eq.-5) were the only process affecting *c-bicarbonate*. The apparent negative correlation between bicarbonate and sulfate *c* values suggests that the *c-bicarbonate* values are indeed reflective of biotransformation processes. The offset of the field estimates from the ideal relationship likely reflects the roles of other electron acceptors in influencing changes in bicarbonate across the plumes.

2.2. Reactive Transport Model Idealization

Several factors will determine the modeled spatial extent of an ideal dissolved hydrocarbon plume emanating from a contaminant source. Among these are the mean groundwater velocity, the dispersion coefficients (reflecting the heterogeneous nature of the subsurface), the mean biotransformation rate, and the source flux term. In the presence of a continuous source of contamination, such as dissolution of sparingly soluble hydrocarbons from a lens of separate phase product, a pseudo-stable plume will develop if biotransformation processes are active. This is because the influx of fresh contaminant mass in the dissolved phase will be balanced at some point by biotransformative losses, integrated across the spatial extent of the plume. Thus, given groundwater data from a number of UST sites, some degree of inverse correlation would be expected between plume length and the vigor of biotransformation processes, the latter reflected by the *c-bicarbonate*. Scatter in this relationship would largely reflect the contributions to variance associated with the other variables.

Wilson, Miller (1978) proposed an analytical solution for solute transport in a homogeneous, infinite aquifer of constant thickness with a uniform fluid flow field, assuming an instantaneous

point source. When integrated over time, the source term is transformed into one of continuous mass injection,

$$c(x, y, t) = \int_{\tau=0}^{\tau=t} \frac{M_f}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-vt)^2}{4D_l\tau} - \frac{y^2}{4D_t\tau} - \lambda\tau\right] d\tau \quad (\text{Eq.-8})$$

where M_f is the mass introduced per unit time, ϕ the porosity, H the aquifer thickness, D_l and D_t the respective longitudinal and transverse dispersion coefficients, v the mean groundwater velocity, λ the first-order decay coefficient, x and y , the spatial coordinates relative to the source location, and t the elapsed time between source introduction and sampling time. Given a set of values for the governing parameters in Eq-8, dissolved hydrocarbon concentrations (e.g., as TPH) may be predicted as a function of space and time. Plume length may be quantified along the longitudinal plume axis by setting $y = 0$ and solving for x , where c equals some prescribed concentration, using a search algorithm (e.g., bisection method).

At (x, y) , the cumulative quantity of dissolved hydrocarbons which have undergone biotransformation, c , is given by superposition according to,

$$c(x, y, t) = \int_{\tau=0}^{\tau=t} \frac{M_f}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-vt)^2}{4D_l\tau} - \frac{y^2}{4D_t\tau} - \lambda\tau\right] d\tau - \int_{\tau=0}^{\tau=t} \frac{M_f}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-vt)^2}{4D_l\tau} - \frac{y^2}{4D_t\tau} - \lambda\tau\right] d\tau \quad (\text{Eq.-9})$$

The generation of excess bicarbonate over background may be estimated at any (x, y) by assuming a representative hydrocarbon composition (e.g., using toluene, C_7H_8 , as a surrogate) and using reaction stoichiometry (Eq.-1 through Eq.-6) to infer the quantity of bicarbonate

generated. A value for *c-bicarbonate* may then be defined in a manner analogous to the field data definition (Eq.-7) by populating the spatial domain associated with a simulated plume with a random distribution of monitoring wells.

At any given site, the values of the parameters in Eq.-8 and Eq.-9 for modeling plume length and *c-bicarbonate* are generally not well known. However, field data and judgment based on practical experience may be used to place constraints on these values in the form of probability distribution functions. These probability distributions may then be used to generate multiple plume realizations through a Monte Carlo simulation approach in which random combinations of model input values are used to compute a distribution of forecast output values. Simulation output consists of a set of plume lengths and associated *c-bicarbonate* values characteristic of the synthetic plume population. The philosophy behind this approach is that, over a large number of sites, the effects of site-specific features such as pronounced physical heterogeneities in the flow field will tend to average together and thus may be represented conceptually by a simple advective-dispersive model. It is essential to recognize that such a model may be quite unsuitable for predicting the behavior of a contaminant plume at an individual site because the simplified model cannot capture the physical and biogeochemical complexities of the subsurface. However, across a number of sites, an idealized model of average plume behavior can provide insights into the relative impacts of different variables on plume behavior.

Probability distribution functions chosen for the governing parameters in Eq.-8 and Eq.-9 are listed on Table 3. Some of the probability distributions were based directly on hydrogeologic data collected from the six sites. For example, mean groundwater velocity was calculated for each site from Darcy's law, using a geometric mean hydraulic conductivity from pumping test

results, a mean annual hydraulic gradient, and an assumed porosity of 0.25. A review of site histories was used to postulate ranges of contaminant influx (i.e., fuel hydrocarbon release volumes) and the length of the source release period. Other parameters could only be postulated in a general sense. For example, longitudinal and transverse dispersivities were assumed to reflect a range of fractional values of the total plume length in each realization (Neumann, Zhang, 1990).

The rate of biotransformation is a key variable because of the effect on both plume length and *c-bicarbonate*. In general, hydrocarbon biotransformation rates are compound-specific and reflect local biogeochemical conditions within a plume (Vroblesky, Chapelle, 1994; Chapelle et al., 1996) and the characteristics of the local microbiological consortia (Borden, Bedient, 1986; Bekins et al., 1998). Nevertheless, from a practical, field-oriented engineering perspective, a simple global first-order kinetic model is often used in site investigations (e.g., Wilson et al., 1995; Buscheck et al., 1996). In this study, a wide range of first-order biotransformation rates, based on values typically reported in the literature and site investigation reports, was assumed for modeling purposes.

A total of 500 Monte Carlo realizations were generated from the probability distributions given on Table 3 using the Crystal Ball add-in package for Microsoft Excel (Decisioneering, Inc., Aurora, Colorado). A simple Basic program was written to solve Eq.-8 for x when $c = 10$ ppb (i.e., plume length) for each realization using the bisection search method. The 10-ppb contour interval was chosen for delineating plume length to maintain consistency with previous studies (e.g., Rice et al., 1995); different definitions of plume length, particularly at much higher concentrations, could conceivably lead to somewhat different results than those presented in this

study. *c-bicarbonate* values were quantified for each synthetic plume using Eq.-7, Eq.-9, and 5 to 15 fictitious monitoring wells at random locations in the vicinity of the plume (Fig. 3).

3. Results and Discussion

Rank-based correlation coefficients illustrating the relationships between model output (plume length and *c-bicarbonate*) and input parameters are given in Table 3. Among the input parameters and the associated probability distributions, variance in groundwater velocity and the biotransformation rate appear to dominate the variance in either model output. Thus, the choices of probability distributions for the other parameters (source term, dispersivities, elapsed time) do not seem to be especially critical in these simulations.

Plume length (defined by the 10 ppb contour) and *c-bicarbonate* are negatively correlated in the synthetic plume population (Fig. 4). Intuitively, this is expected since low biotransformation rates tend to produce longer plumes and low *c-bicarbonate* values, whereas the opposite is expected for high biotransformation rates. The extreme values present at either end of the graph reflect biotransformation rates on the tails of the distribution, coupled with particular chance combinations of the other variables. The relationship between plume length and *c-bicarbonate* is also shown for the six field sites. The field data and synthetic plume metrics are generally in good agreement with one another. The notable exception is the plume associated with the PMCB site, which appears to be too short given the observed *c-bicarbonate* value. However, this plume is truncated by discharge into a creek approximately 30 m downgradient from the source area. In the absence of the creek, the plume would be expected to extend further and thus would plot more toward the centerline shown on Fig. 4.

The forecast relationship between the biotransformation rate, k , and c -bicarbonate is shown on Fig. 5a. An overall positive trend is apparent in the forecasts, although a great deal of scatter exists in the relationship. Assuming a lognormal distribution of c -bicarbonate for the field data collected from the six sites, the values bracketed by one standard deviation range from 67 mg/L to 215 mg/L. The corresponding range of k -values in the synthetic plume set (bracketed by one standard deviation) falls between 4×10^{-4} and $7 \times 10^{-3} \text{ day}^{-1}$, with a geometric mean of $1.6 \times 10^{-3} \text{ day}^{-1}$. According to the model, k values above or below this interval would generally produce plumes with c -bicarbonate values that would fall outside of those commonly observed in the field.

By itself, the constraint imposed on k by c -bicarbonate is tenuous because of the many simplifying assumptions in the model and the definition of c -bicarbonate itself (Eq.-7). However, plume length serves as an additional model output metric that can be used as an independent check on the general role of biotransformation, manifested as k , in influencing plume behavior. The modeled relationship between k and plume length is shown on Fig. 5b. An overall negative trend is apparent in this forecast, again with considerable scatter. Assuming a lognormal distribution of plume lengths (defined by the 10 ppb TPH contour) among the six sites, the values bracketed by one standard deviation range from 56 m to 394 m. The corresponding range of k -values in the synthetic population (bracketed by one standard deviation) falls between 4×10^{-4} and $9 \times 10^{-3} \text{ day}^{-1}$, with a geometric mean value of $1.9 \times 10^{-3} \text{ day}^{-1}$.

Considering the broad simplifying assumptions inherent in the modeling and the uncertainties in model parameters, the close agreement for the range of k -values that are consistent with field

data in terms of *c-bicarbonate*, as well as plume length, may well involve an element of chance. Nevertheless, the model does suggest a range of average biotransformation rates on the order of 3×10^{-4} to $9 \times 10^{-3} \text{ day}^{-1}$ for the selected sites. Values of λ outside of this range would be expected to yield *c-bicarbonate* and plume lengths that are not consistent with observation. Moreover, this range of values is consistent with first-order reaction rates for fuel hydrocarbon compounds estimated in other field studies. A review of published field-derived benzene biotransformation rates under a variety of biogeochemical regimes (Table 4) indicates a geometric mean value of $3 \times 10^{-3} \text{ day}^{-1}$, with a range encompassed by one standard deviation (lognormal distribution) of 4×10^{-4} to $3 \times 10^{-2} \text{ day}^{-1}$ (Fig. 6).

Clearly, biotransformation of fuel hydrocarbons through microbially-mediated sequential redox reactions in heterogeneous aquifers entails a complex set of phenomena that cannot be adequately captured by a simple, linear, homogeneous analytical solution for individual real aquifers. The advantage of pooling data from multiple sites is that general trends may be identified despite effects of site-specific features (e.g., physical and chemical heterogeneities, complex source terms and boundary conditions) that can complicate data interpretation at individual sites. In other words, interpretation of the data takes the form of statistical trends across groups of sites as opposed to detailed, deterministic predictions of plume behavior in selected case examples. Under this philosophy, idealized analytical solutions to the advective-dispersive transport equation, which essentially represent expected “average” plume behavior, are highly suitable for this type of analysis when combined with a Monte Carlo simulation approach. Indeed, the practical utility in studies conducted in this manner is to provide support for establishing or revising regulatory frameworks by distilling information from field sites into simplified relationships. Regulatory agencies are charged with formulating policy to be applied

to broad classes of sites. As such, broad trends in data across multiple sites are in some ways more valuable than anecdotal findings from detailed case studies.

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Table 1. Sites included in study.

LUFT site location	Hydrogeologic setting	Contaminant	Number of monitoring wells	Plume length (m)	Analytes
Camp Pendleton Marine Corps Base (PMCB)	Coastal canyon alluvium and fill	Gasoline	16	30	TPH, BTEX, HCO_3^- (as alkalinity), CH_4 , E_h , Fe^{2+} , O_2 , NO_3^- , pH, SO_4^{2-}
Castle Air Force Base (CAFB)	Broad alluvial plain	Aviation fuel (JP-4)	19	210	TPH, BTEX, HCO_3^- (as alkalinity), CH_4 , E_h , Fe^{2+} , Mn^{2+} , O_2 , NO_3^- , pH, SO_4^{2-}
George Air Force Base (GAFB)	High desert alluvial fan	Aviation fuel (JP-4)	16	610	TPH, BTEX, HCO_3^- (as alkalinity), CH_4 , E_h , Fe^{2+} , Mn^{2+} , O_2 , NO_3^- , pH, SO_4^{2-}
Presidio of San Francisco (PSF)	Shallow marine deposits, organic-rich	Gasoline and diesel	13	180	TPH, BTEX, HCO_3^- (as alkalinity), CH_4 , E_h , Fe^{2+} , Mn^{2+} , O_2 , NO_3^- , pH, SO_4^{2-}
Travis Air Force Base (TAFB)	Broad alluvial plain	Gasoline	29	120	TPH, BTEX, HCO_3^- (as alkalinity), CH_4 , E_h , Fe^{2+} , Mn^{2+} , O_2 , NO_3^- , pH, SO_4^{2-}
Vandenberg Air Force Base (VAFB)	Shallow marine deposits	Gasoline	14	120	TPH, BTEX, HCO_3^- (as alkalinity), CH_4 , E_h , Fe^{2+} , Mn^{2+} , NO_3^- , pH, SO_4^{2-}

Table 2. LUFT site geochemical indicator data (concentrations given in mg/L).

Species	Zone	PMCB	CAFB	GAFB	PSF	TAFB	VAFB
O ₂	Plume	0.65	2.1	3.4	0.4	0.2	n.a.
	Background	1	2.9	6.4	0.3	0.5	n.a.
	Δc	-0.35	-0.8	-3.0	0.1	-0.3	n.a.
NO ₃ ⁻	Plume	1.6	2.8	0.3	0.01	0.3	0.05
	Background	3.2	6.5	1.4	0.06	5.5	0.07
	Δc	-1.6	-3.7	-1.1	-0.05	-5.2	-0.02
SO ₄ ²⁻	Plume	70.4	15.9	53	10.2	456	3.9
	Background	84	27.1	137.5	48.3	740	200
	Δc	-13.6	-11.2	-84.5	-38.1	-284	-196.1
Fe ²⁺	Plume	1.5	0.05	0.05	4.7	2.97	3.3
	Background	0	0.007	0	0.03	0.02	0.8
	Δc	1.5	0.043	0.05	4.67	2.95	2.5
Mn ²⁺	Plume	n.a.	0.88	1.5	0.78	2.9	0.50
	Background	n.a.	0.5	0	0.43	0.2	0.22
	Δc	n.a.	0.38	1.5	0.35	2.7	0.28
†HCO ₃ ⁻	Plume	466	262	252	500	621	500
	Background	393	182	176	383	327	300
	Δc	73	80	76	117	294	200
CH ₄	Plume	0.9	0.006	0.002	7	0.21	0.26
	Background	0.006	0.0006	0.0002	0.3	0.005	0.004
	Δc	0.9	0.0054	0.0018	6.7	0.205	0.256

* n.a. = data not available.

† Reported as bicarbonate alkalinity.

Table 3. Probability distributions used in Monte Carlo realizations.

Parameter	*Probability distribution	Basis	R (Plume length)	R(Δc_{alk})
[†] Source term (M_f)	18,900 - 151,400 liters	Postulated.	0.08	0.09
[‡] Aquifer thickness (H)	4.6 ± 1.5 m	Site hydrostratigraphies.	-0.04	-0.13
Groundwater velocity (v)	0.003 - 1.0 m/day	Estimated mean hydraulic conductivities by pumping tests; interpolated mean hydraulic gradient, Darcy's law.	0.68	-0.69
Degradation coefficient (λ)	0.01% - 2% day ⁻¹	Postulated based on commonly reported range in the literature.	-0.57	0.35
[§] L:L ratio	0.03 - 0.33	Assumed dispersivity to plume length scale ratio.	0.13	-0.02
T:L ratio	0.003 - 0.03	Assumed dispersivity to plume length scale ratio.	-0.03	-0.11
** Elapsed time since source initiation (t)	20 - 40 years	Site histories.	0.09	-0.12

* Unless otherwise indicated, probability distributions are lognormal, with the range between the 5th percentile and 95th percentile shown.

[†] Volumetric flux of free product converted to dissolved mass by assuming (1) 10% of free product dissolves, and (2) density of free product = 0.8 g/cm³.

[‡] Normal distribution given (mean ± standard deviation).

[§] Longitudinal dispersivity, α_L , was determined by applying this ratio to the forecast plume length in an iterative manner. The longitudinal dispersion coefficient, D_L , was computed through the relationship $D_L = \alpha_L v$. Transverse dispersivity, α_T , and the transverse dispersion coefficient, D_T , were quantified in an analogous manner.

****** Uniform distribution given (minimum and maximum).

Table 4. Selected published reaction rates for benzene estimated from field data at groundwater contamination sites.

Conditions	Rate (day⁻¹)	Reference
Iron-reducing.	1.1×10^{-4}	Wilson et al., 1996
Iron-reducing.	2.0×10^{-4}	Rifai et al., 1995
Nitrate-reducing, sulfate-reducing, and methanogenic.	4.3×10^{-4}	Wilson et al., 1994b
Nitrate-reducing.	9.0×10^{-4}	Borden et al., 1997
Iron-reducing.	2.2×10^{-3}	Wilson et al., 1996
Methanogenic.	7.1×10^{-3}	Wilson et al., 1990
Sulfate-reducing.	1.8×10^{-2}	Wiedemeier et al., 1995
Methanogenic.	1×10^{-2}	Wiedemeier et al., 1995
Methanogenic, iron-reducing, manganese-reducing.	1.7×10^{-2}	Cozzarelli et al., 1990
Sulfate-reducing.	2.8×10^{-2}	Wiedemeier et al., 1996
Sulfate-reducing.	3.8×10^{-2}	Wiedemeier et al., 1996

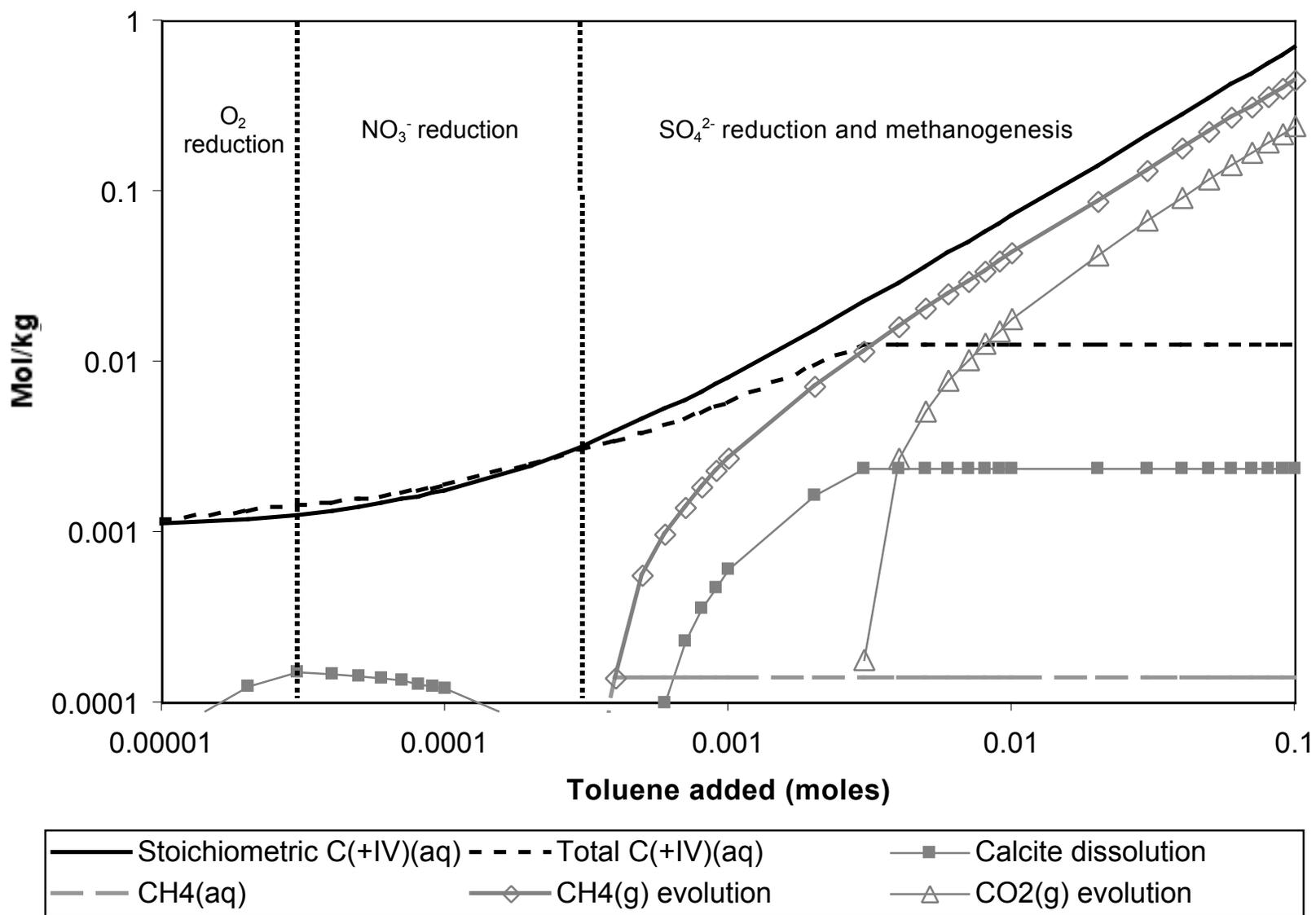


Figure 1. Carbon mass balance predicted by PHREEQC for toluene mineralization in a hypothetical groundwater composition, with C(+IV) referring to aqueous inorganic carbon (valence state of +4). Stoichiometric C(+IV) reflects the amount of inorganic carbon that would be present in solution if all of the toluene were converted exclusively into aqueous phase C(+IV). In reality, some is evolved from solution as CO_2 and CH_4 gases, with some CH_4 remaining in solution. Dissolution of small quantities of $CaCO_3$ also exerts a minor influence on aqueous C(+IV).

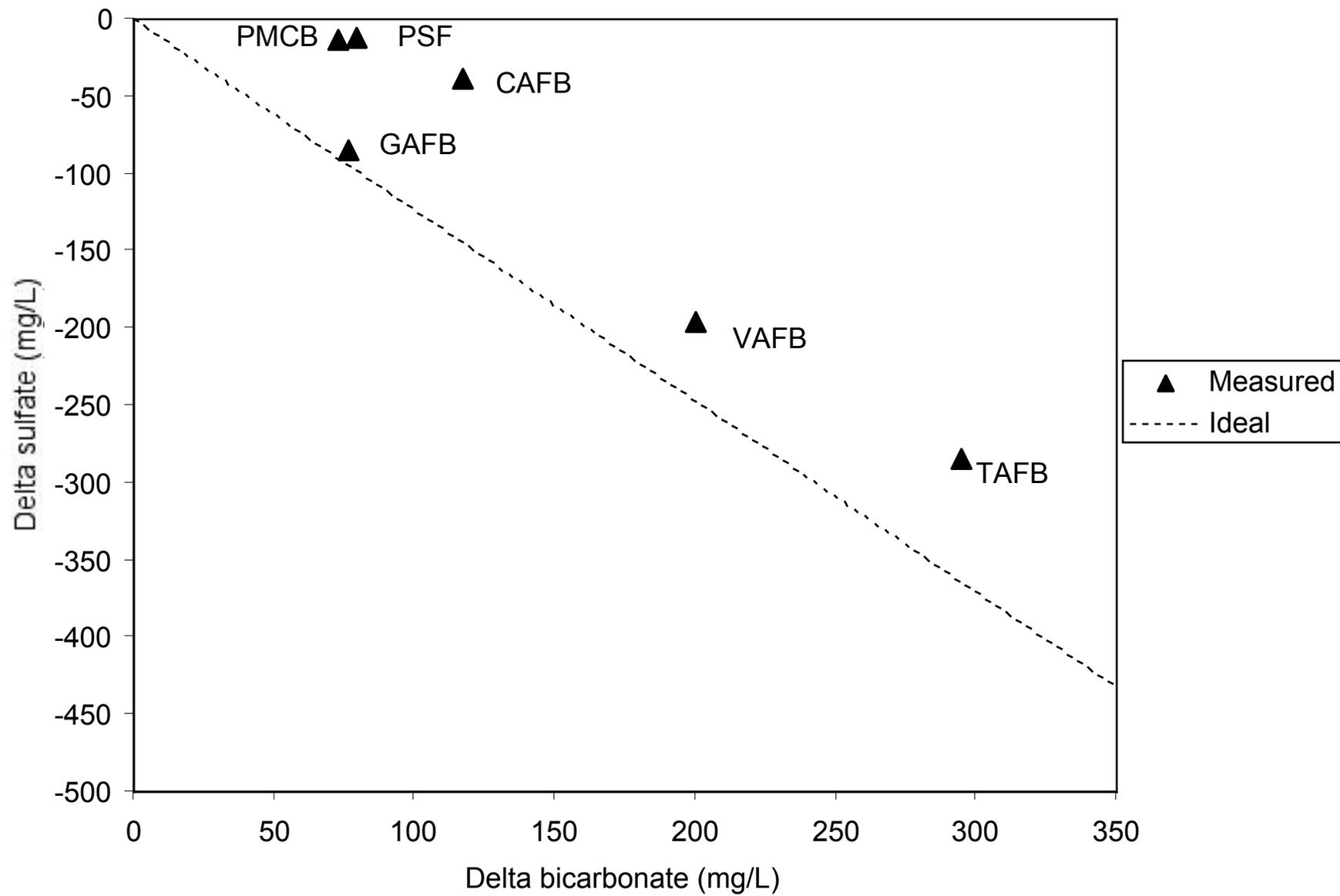


Figure 2. Relationship between δ -sulfate and δ -bicarbonate.

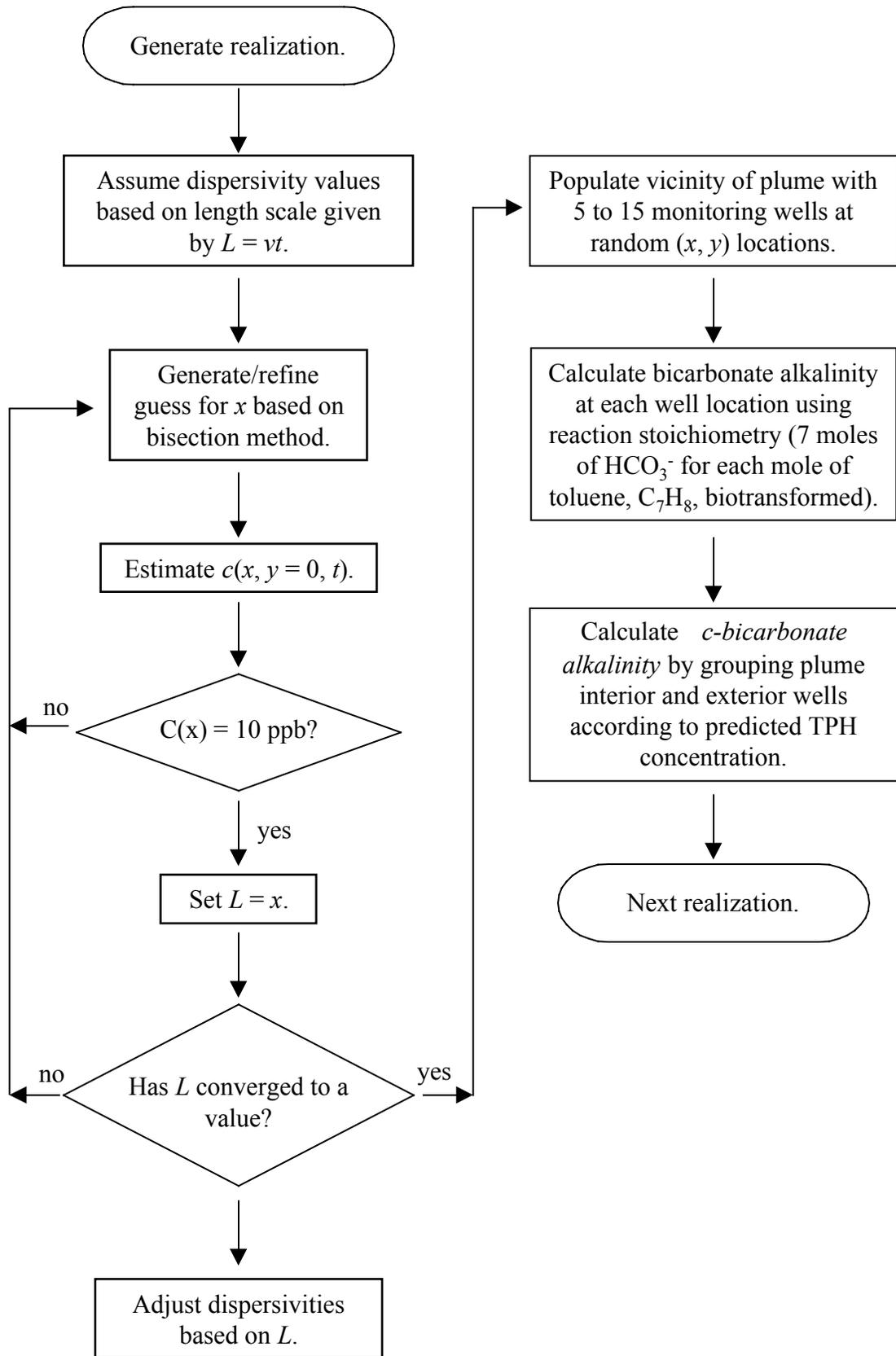


Figure 3. Computational scheme for generation of synthetic plume population. L refers to plume length as defined by the distance from the source downgradient to the 10-ppb contour along the plume centerline.

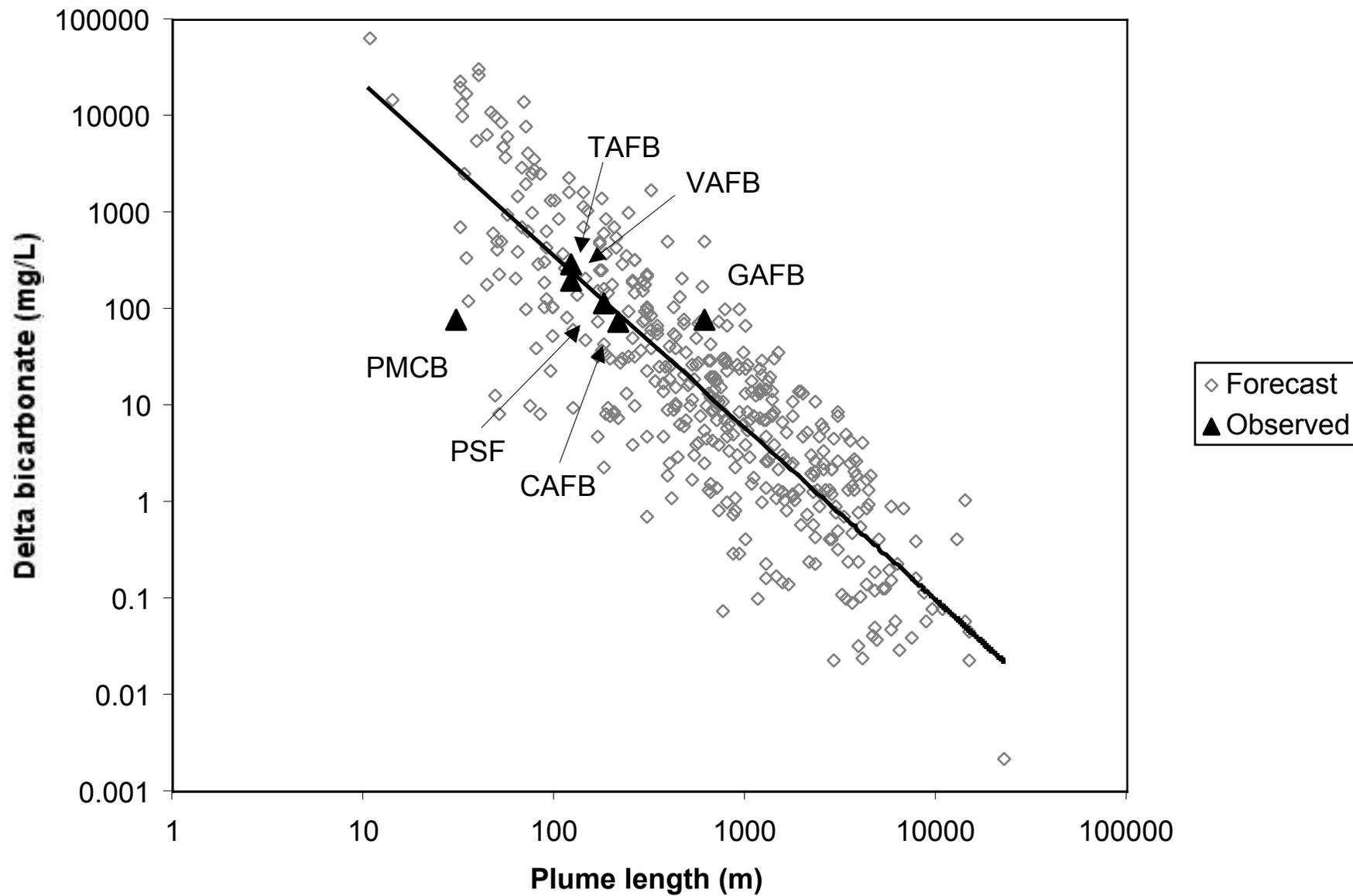


Figure 4. Relationship between plume length and *c*-bicarbonate.

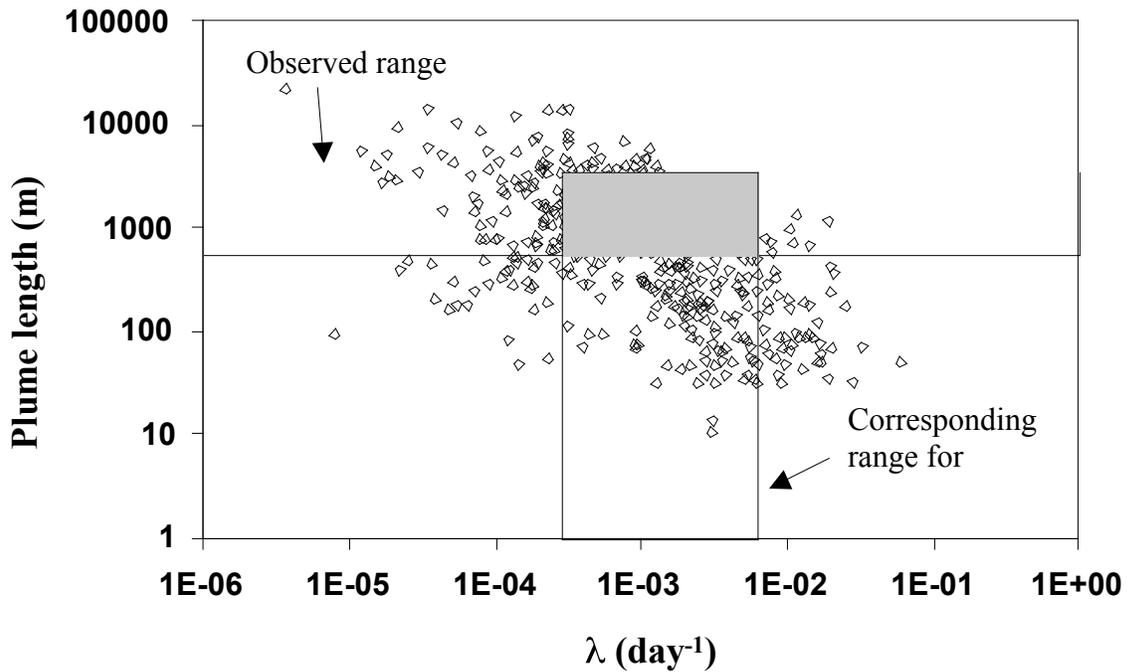
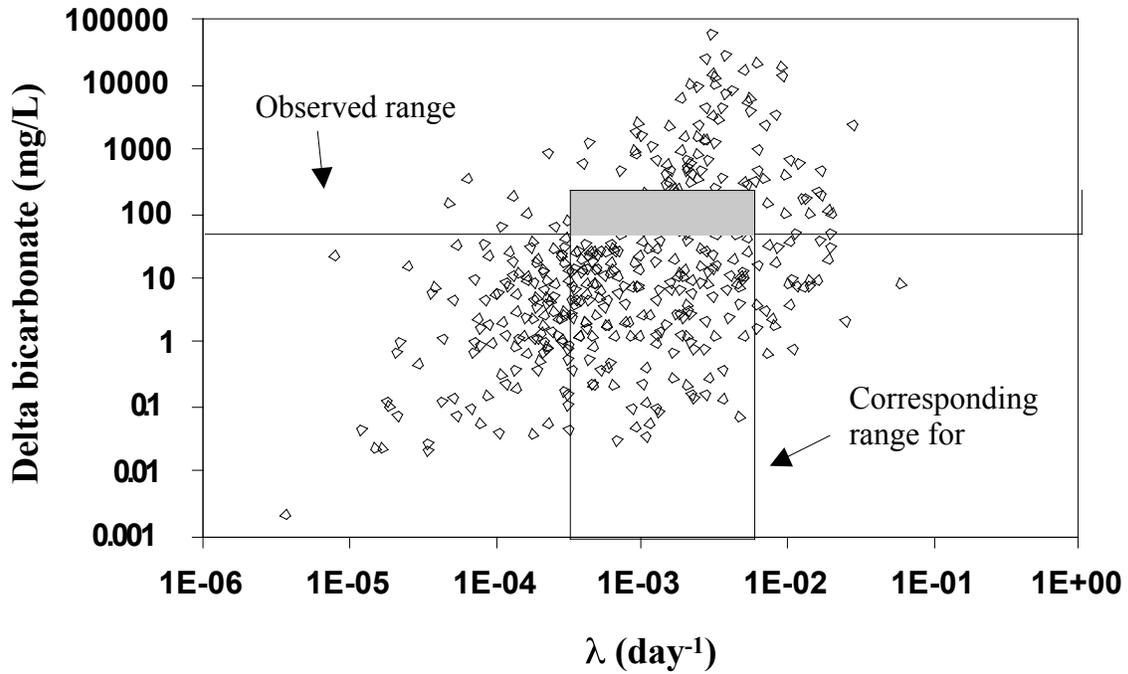


Figure 5. Simulated relationships between (a) *c*-bicarbonate and degradation rate (λ), top, and (b) plume length and degradation rate, bottom. Each data point represents a simulated plume with a particular *c*-bicarbonate, degradation rate, and plume length. The indicated range in the independent variable reflects the standard deviation of log-transformed λ values that correspond to those simulated data points falling within the standard deviation range of the log-transformed dependent variable (*c*-bicarbonate or plume length).

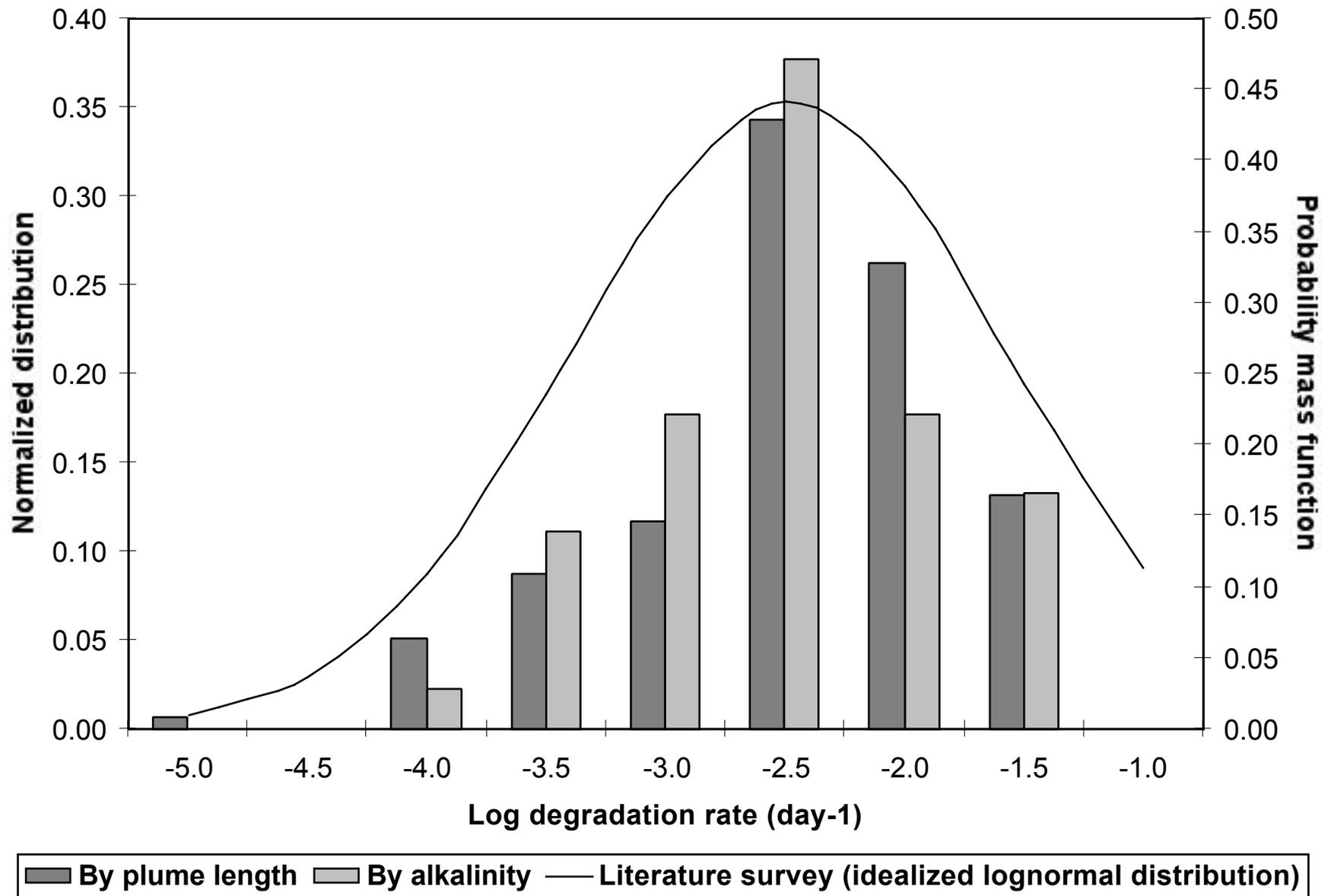


Figure 6. Probability distribution of biotransformation rates: best-fit lognormal distribution of literature values for benzene compared to values for TPH obtained in this study from Δc -bicarbonate and plume length analyses.

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